

Since $\omega_0 \approx f_l \lambda_p / d$, where f_l is the focal length of the focus lens (≈ 15 cm) and d is the input spot diameter of the dye laser (≈ 1 mm), ω_0 is calculated to be $\sim 70 \mu$. Thus $\pi \omega_0^2 / \lambda_p$ is ~ 3.4 cm. As mentioned in the text, the length of the vapor zone is ~ 2 to 3 cm.

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Stark-Induced Three-Wave Mixing in Molecular Gases—Part I: Theory

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Abstract—Application of a dc electric field to a gaseous system destroys the basic inversion symmetry and allows three-wave mixing processes to occur. A theoretical derivation of this effect under conditions of resonantly enhanced nonlinearities is given for a three-level system. Calculations are presented for mixing of a CO₂ laser with 4-GHz microwaves in the molecule NH₂D, producing single lower sideband radiation.

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I. INTRODUCTION

NONLINEAR optical mixing in atomic vapors has been demonstrated for a number of different processes including third harmonic generation [1]-[4], dc-induced second-harmonic generation [5], [6], infrared upconversion [7], [8], and multiphoton generation of new wavelengths [9]. Resonant enhancement and phase matching of three-photon processes has led to rather impressive conversion efficiencies for certain interactions in atomic vapors [2]-[4]. In this paper we discuss three-wave mixing processes in molecules where resonant enhancement is achieved via Stark tuning of the molecular energy levels. This interaction and its subsequent experimental observation [10] suggest a new type of

electrooptical effect, namely single-sideband generation by applied microwave frequencies. A theoretical derivation and calculations of the interaction for a three-level system are presented here, specialized to the case of a particular molecule (NH_2D). The experimental observations are discussed in the following paper [10].

II. THEORY

The application of a dc electric field to a gas introduces a preferred spatial direction, thus destroying the inversion symmetry. The second-order-induced polarization amplitude can then be related to the product of the field (complex) amplitudes by

$$P_{\alpha}^{\omega_1=\omega_3-\omega_2} = d_{\alpha\beta\gamma}^{\omega_1=\omega_3-\omega_2} E_{3\beta} E_{2\gamma}^* \quad (1)$$

Choosing the direction of the dc field as z , the allowed $d_{\alpha\beta\gamma}$ are d_{zzz} , d_{zzi} , and d_{izi} , where $i = x$ or y .

In searching for a candidate gas in which to observe the effect, one should look for: 1) molecules with a strong permanent dipole moment or 2) molecules which, in the presence of a dc field, acquire a large dipole moment so that the presence of the dc field constitutes an appreciable perturbation.

A molecule meeting criterion 2) is NH_2D . The molecule has, among others, the three levels shown in Fig. 1, which can be Stark-tuned into simultaneous resonance with the $P(20)$ line of the CO_2 laser [11]–[14] and microwave radiation near 4 GHz as shown. This should lead to a strong resonant mixing of the $P(20)$ line (of frequency $\omega_3/2\pi$) and the microwave field at $\omega_2/2\pi = 4$ GHz, giving rise to the difference frequency radiation at $\omega_1 = \omega_3 - \omega_2$ when the Stark field is near $E_{dc} = 3570$ V/cm. Levels 1 and 2 belong to the lowest vibrational state ($\nu_2 = 0$) and have molecular angular momentum quantum numbers $J = 4$ and $|M| = 4$. The subscripts 04 and 14 correspond to the standard asymmetric top designation [15]. The symbols a (asymmetric) and s (symmetric) refer to the parity of the inversion-split vibrational wave functions. The application of an electric field E_{dc} causes an admixture of the wave functions $|4_{04}a\rangle$ and $|4_{14}s\rangle$ which is due to a nonvanishing matrix element of the molecular dipole operator connecting the two states. This admixture, which will soon be shown to be responsible for the nonlinear mixing, disappears at zero dc field. The parameter Δ appearing in the expression for the wave functions corresponds to the energy splitting $E_2 - E_1$ between the two low-lying states and is given by

$$\Delta = [4|\langle 4_{04}a|\mu_z|4_{14}s\rangle|^2 (E_{dc})^2 + \delta^2]^{1/2} \quad (2)$$

while the admixture wave functions are

$$|1\rangle = \frac{1}{\sqrt{2}} [\sqrt{1+\delta/\Delta} |4_{04}a\rangle + \sqrt{1-\delta/\Delta} |4_{14}s\rangle],$$

$$|2\rangle = \frac{1}{\sqrt{2}} \left[\sqrt{1-\delta/\Delta} |4_{04}a\rangle - \sqrt{1+\delta/\Delta} |4_{14}s\rangle \right]$$

where δ is the zero field splitting and μ_z is the projection of the molecular dipole moment operator along the direction of the dc field.

The expression for the nonlinear dipole moment of an NH_2D molecule depends on matrix elements which can be

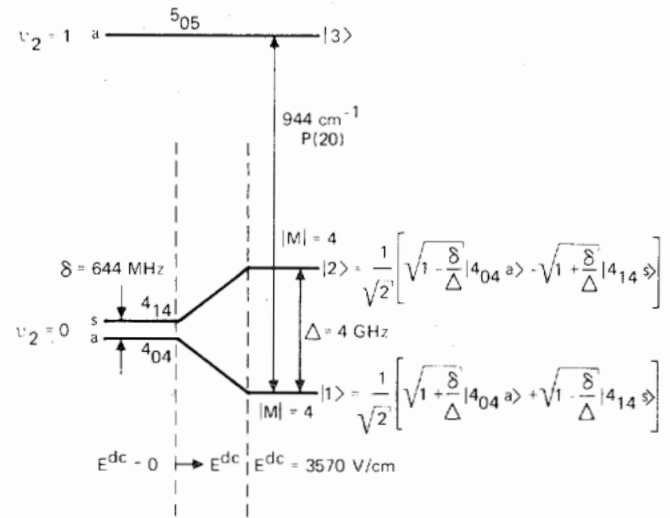


Fig. 1. Some of the energy levels relevant to the derivation of the nonlinear coefficient.

determined from linear absorption data as well as from the data on Stark splitting. This makes possible, in principle, a precise theoretical derivation of the nonlinear mixing behavior of this molecule and of its parametric dependencies.

Applying second-order perturbation theory [16, p. 556] to the three-level system of Fig. 1, and keeping only the resonant (i.e., with near vanishing denominator) term, leads to the following expression for the polarization generated at $\omega_1 = \omega_3 - \omega_2$ by the applied fields at ω_2, ω_3 :

$$P_{\alpha}^{(2)}(t) = \frac{1}{4\hbar^2} \left\{ \frac{N_1(\bar{\mu} \cdot \bar{E}_3)_{13}(\bar{\mu} \cdot \bar{E}_2^*)_{21}(\mu_{\alpha})_{32}}{[\Gamma_{13} + i(\omega_3 - \omega_{31})][\Gamma_{32} + i(\omega_1 - \omega_{32})]} - \frac{(N_2 - N_1)(\bar{\mu} \cdot \bar{E}_3)_{13}(\bar{\mu} \cdot \bar{E}_2^*)_{21}(\mu_{\alpha})_{32}}{[\Gamma_{12} + i(\omega_2 - \omega_{21})][\Gamma_{32} + i(\omega_1 - \omega_{32})]} \right\} \cdot \exp(i\omega_1 t) + \text{c.c.} \quad (3)$$

where N_i is the population density of level i with $E_2 = E_3 = 0$. At thermal equilibrium $N_2 \approx N_1$, and the main contribution to $P_{\alpha}^{(2)}$ is from the first term, the one proportional to N_1 .

At zero dc field the matrix element $(\mu_{\alpha})_{32}$ is zero. This is due to the fact that, as can be shown by group theoretic arguments, only the molecular dipole moment along the b of NH_2D axis (μ_b) may possess a nonvanishing matrix element $\langle 5_{05}a|\mu_b|4_{14}s\rangle$, but $\mu_b = 0$ due to the basal plane symmetry of NH_2D . It follows from (3) that for $E_{dc} = 0$ no frequency mixing takes place. When $E_{dc} \neq 0$ the ground state wave function $|4_{04}a\rangle$ is admixed into level 2 as shown in Fig. 1. This results in a nonvanishing matrix element $(\mu_{\alpha})_{32}$ proportional to $\langle 5_{05}a|\mu_a|4_{04}a\rangle$.

For $\bar{E}_2 \parallel \hat{z}$, $\alpha = x$, and $\bar{E}_3 \parallel \hat{x}$ we find, using the admixed wave functions, that the triple matrix element product appearing in (3) is given by

$$(\mu_z)_{21}(\mu_x)_{13}(\mu_x)_{32} = -4\mu_c \langle 4_{04}a|\mu_x|5_{05}a\rangle^2 \cdot E_{dc} M^2 \left(\frac{\delta}{\Delta^2} \right) \quad (4)$$

The dependence of the triple matrix element product on the dc electric field is contained in the factor $E_{dc} \delta/\Delta^2$ with Δ the

energy separation between levels 2 and 1, as given by (2). The nonlinear mixing is thus absent, i.e., $P_x^{(2)} = 0$, at zero field ($E_{dc} = 0$) and at very high fields ($\Delta \gg \delta$). From (1) and (3) and using the fact that at room temperature $N_2 \cong N_1$, we obtain

$$d_{\alpha\beta\gamma}^{\omega_1=\omega_3-\omega_2} = \frac{1}{2\hbar^2} \frac{N_1(\mu_\gamma)_{21}(\mu_\beta)_{13}(\mu_\alpha)_{32}}{[\Gamma_{13} + i(\omega_3 - \omega_{31})][\Gamma_{32} + i(\omega_1 - \omega_{32})]} \quad (5)$$

Expression (5) applies to stationary molecules with energy levels at E_1 , E_2 , and E_3 . In a gas sample we need to account for the Doppler shift of the transition energies of individual molecules. This is done by averaging the nonlinear coefficient $d_{\alpha\beta\gamma}$ over the Maxwellian velocity distribution with the result, for operation at line center, that

$$d_{\alpha\beta\gamma}^{\omega_1=\omega_3-\omega_2} = \frac{-N_1(\mu_\gamma)_{21}(\mu_\beta)_{13}(\mu_\alpha)_{32}}{2\hbar^2} \cdot \sqrt{\pi/2} \frac{c}{\sigma\omega_{31}} \frac{\partial F(x)}{\partial \Gamma} \quad (6)$$

where

$$F(x) = e^{x^2} \operatorname{erfc}(x), \quad \omega_{31} \approx \omega_{32} \gg \omega_{21}, \quad \Gamma_{13} \approx \Gamma_{32} \equiv \Gamma, \\ \sigma = \sqrt{kT/M}$$

is the rms molecular velocity, and $x = c\Gamma/(\sqrt{2}\sigma\omega_{31})$ is the ratio of the homogeneous (spontaneous plus pressure) line-width Γ to the Doppler linewidth $\sqrt{2}\sigma\omega_{31}/c$.

Although a numerical estimate of the nonlinear mixing coefficient based on (6) is possible, a safer procedure, and one that serves as a check on the matrix elements needed to evaluate d_{xxz} (the largest coefficient in NH_2D) is to relate it to the linear absorption coefficient of x polarized field at $\omega_3 = \omega_{31}$. The latter can be shown to be given (in esu units) by

$$\gamma_{31} = \gamma_H \sqrt{\pi} x e^{x^2} \operatorname{erfc}(x) \quad (7)$$

where γ_H is the value of γ_{31} at high pressures ($c\Gamma \gg \sigma\omega_{31}$) and is given by

$$\gamma_H = \frac{4\pi|\mu_{13}|^2\omega_{31}}{\hbar c\Gamma} N_1.$$

Combining (6) and (7) leads after some mathematical manipulation to

$$d_{xxz}^{\omega_1=\omega_3-\omega_2} = -\frac{c(\mu_z)_{12}}{8\pi\hbar\omega_{31}} \left(\frac{\mu_{23}}{\mu_{13}} \right) \cdot \sqrt{\frac{\pi}{2}} \frac{c\gamma_H}{\sigma\omega_{31}} \left[2x^2 F(x) - \frac{2}{\sqrt{\pi}} x \right]. \quad (8)$$

The various constants in (8) are evaluated as follows: the matrix element $(\mu_z)_{12}$ is a function of the admixture and according to the wave functions (2) is given by

$$(\mu_z)_{12} = \frac{\delta}{\Delta} \langle 4_{04}a|\mu_z|4_{14}s \rangle. \quad (9)$$

We obtain the matrix element $\langle a|\mu_z|s \rangle$ from comparing the splitting $E_2 - E_1$, as given by (2) to the experimental tuning

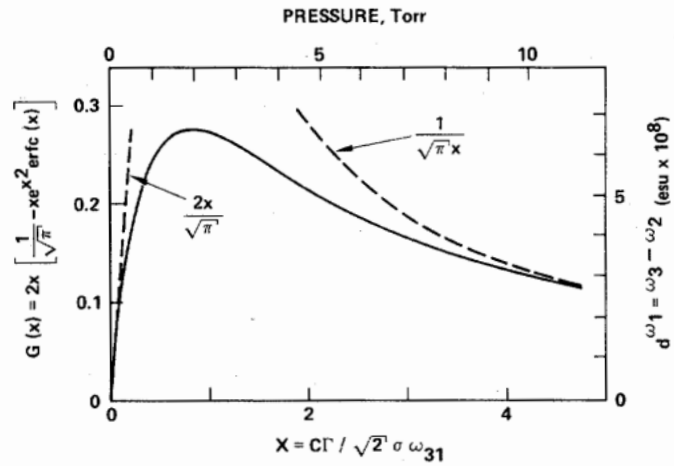


Fig. 2. Theoretical dependence of NH_2D nonlinear coefficient on pressure when the applied fields are exactly resonant with the Stark-tuned energy levels.

curve of $E_2 - E_1$ versus E_{dc} [14]. This yields $\langle a|\mu_z|s \rangle = 1.14 \times 10^{-18}$ esu. At resonance $E_{dc} = 3570$ V/cm and $\delta/\Delta = 0.174$. These data are used in (9) and result in

$$(\mu_z)_{12} = 0.174 \langle a|\mu_z|s \rangle = 0.198 \times 10^{-18} \text{ esu}.$$

The saturated absorption γ_H and pressure broadening coefficient are obtained from the data in [13] as

$$\gamma_H = 0.028 \text{ cm}^{-1}$$

$$\Gamma/P = 2\pi(20.1 \text{ MHz/torr}).$$

With these data we obtain

$$d_{xxz}^{\omega_1=\omega_3-\omega_2} = 2.31 \times 10^{-7} G(x) \text{ esu} \quad (10)$$

$$G(x) = 2x \left[\frac{1}{\sqrt{\pi}} - x e^{x^2} \operatorname{erfc}(x) \right]. \quad (11)$$

The theoretical dependence of d_{xxz} on pressure [see (10)] is plotted in Fig. 2. The peak occurs at $P = 2$ torr and has a value of

$$(d_{xxz}^{\omega_1=\omega_3-\omega_2})_{\max} = 6.4 \times 10^{-8} \text{ esu} = 2.4 \times 10^{-22} \text{ MKS}.$$

A comparison of this predicted behavior with experiment is given in [10].

The coefficient d estimated above refers to the generation of sideband radiation at ω_1 by mixing a CO_2 $P(20)$ line with a microwave field ω_2 (at 4.1 GHz). It is thus appropriate to compare it to the electrooptic coefficient r_{41} of GaAs which can be used, alternatively, to generate the sideband by conventional electrooptic modulation.

Using the correspondence [16, ch. 16]

$$r_{jlk} = -\frac{2\epsilon_0}{\epsilon_j \epsilon_l} d_{jkl} \quad (12)$$

we have

$$\frac{(n^3 r)_{\text{NH}_2\text{D}}}{(n^3 r)_{\text{GaAs}}} \sim 0.8. \quad (13)$$

We thus reach the conclusion that for sideband generation, dc-biased NH_2D at $P \approx 2$ torr is comparable to GaAs (which is

one of the best infrared modulation materials). We must recognize, however, that this large coefficient was obtained by exploiting the resonant nature of the effect. The penalty we pay for this is that of reduced bandwidth.

III. CONCLUSIONS

In conclusion, we have shown in detail how Stark admixing can give rise to second-order optical nonlinearities in gases. We have derived an expression for the coefficient describing the mixing of an infrared and a microwave field in NH_2D . Available absorption data were used to obtain a numerical estimate for the mixing and to describe its parametric dependence. An experimental demonstration of this effect is described in the following paper [10].

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Stark-Induced Three-Wave Mixing in Molecular Gases—Part II: Experiment

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Abstract—The first observation of resonantly enhanced, dc-induced, three-wave mixing in a gas is presented. A CW CO_2 laser beam and microwave radiation at 4 GHz are mixed in a microwave Stark cell containing gaseous NH_2D . A single new sideband, 4 GHz below the applied CO_2 laser frequency, is observed with the aid of a scanning Fabry-Perot interferometer. The dependence of the sideband signal on gas pressure, microwave frequency, applied dc field, and microwave power are presented and compared with theoretical predictions.

I. INTRODUCTION

IN the accompanying paper [1] it was predicted that a resonantly enhanced nonlinear mixing process in the molecule NH_2D could be induced by application of a dc electric field,

where CO_2 laser radiation and microwave energy at 4 GHz interact producing a new single sideband 4 GHz below the applied laser frequency. We report here the first experimental observation of such single-sideband optical modulation, unambiguously identified through the use of a scanning Fabry-Perot interferometer (SFP). We present measurements of the dependence of the parametric signal on gas pressure, microwave frequency, applied dc field, and microwave power. The results are all in good agreement with theoretical predictions although there is some uncertainty in the quantitative comparisons due to undetermined coupling losses in the microwave structure. Qualitatively, the agreement is excellent.

II. EXPERIMENTAL APPARATUS

The experimental apparatus for the observation of the interaction is discussed with reference to Fig. 1. A frequency-stabilized CW CO_2 laser beam (operating at $P(20)$ line center)

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